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(54) Title: HALOGEN-FREE POLYMERIC COMPOSITIONS

(57) Abstract: The present invention relates to a halogen-free polymeric composition including: (a) at least two metallocene catalysed olefin polymers and/or copolymers wherein at least one of the olefin polymers and/or copolymers is elastomeric; and (b) an effective amount of at least one filler which is capable of providing the polymeric composition with flame retardant properties substantially similar to that of plasticised PVC. The invention also relates to a process for preparing the halogen-free polymeric composition and articles which are composed wholly or partly of the halogen-free polymeric composition.

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HALOGEN-FREE POLYMERIC COMPOSITIONS

The present invention relates to halogen-free polymeric compositions that are capable of acting as a substitute and/or enhancement to halogenated thermoplastics such as plasticised polyvinyl chloride (PVC), especially in the production of electrical cables, power cables, building parts and wires, communication cables and automotive parts.

Plasticised PVC is used in a large range of applications, including cable insulation and sheathing, floor coverings, artificial leather and sound insulation. PVC, and especially plasticised PVC, is easily processed and readily extruded to provide, for example, sheathing for cables, etc. Another intrinsic property of plasticised PVC is its ability to retard the spread of flames. When exposed to fire, plasticised PVC decomposes producing hydrochloric acid, which has the effect of starving the burning material of oxygen. However, the acrid fumes produced sometimes cause more problems than the fire itself through corrosion and smoke formation. Plasticised PVC is also a good electrical insulator even when plasticised hence its suitability for use as electrical cable insulation and sheathing.

Attempts to modify the properties of polyolefins such as polyethylene have been made in order to provide a substitute for polyvinyl chloride, especially as sheathing for electrical cable. Hydrocarbon oil has been added in some cases to copolymers based on polyolefins in order to improve their flexibility. However, the addition of hydrocarbon oil increases flammability and requires the addition of considerably more flame retardant in order to match the flame retardant properties of plasticised PVC. Polysiloxanes may also be added to ethylene, butyl acrylate and ethylene ethyl acrylate copolymers containing low cost mineral fillers. However, the addition of a polysiloxane makes the compound more expensive than plasticised PVC. The polysiloxane is needed to achieve a basic flame

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retardance. In addition, it tends to migrate or separate to the surface and form a skin that is observable. Furthermore, having migrated to the surface, the polysiloxane can be removed by abrasion resulting in the  
5 reduction or loss of flame retardance.

Similarly, aluminium hydroxide and/or magnesium hydroxide have been added to copolymers of ethylene and vinyl acetate to produce polymeric compositions having similar properties to plasticised PVC. However, aluminium  
10 hydroxide and magnesium hydroxide are intrinsically more expensive in the proportions necessary to provide appropriate flame retardance and add considerably to the cost.

A requirement accordingly exists to provide a  
15 polymeric composition with similar properties to plasticised PVC but without decomposing to produce acrid fumes when exposed to fire.

Accordingly, the present invention provides a halogen-free polymeric composition including:

- 20 (a) at least two metallocene catalysed olefin polymers and/or copolymers wherein at least one of the olefin polymers and/or copolymers is elastomeric; and  
(b) an effective amount of at least one filler which is capable of providing the polymeric composition  
25 with flame retardant properties substantially similar to that of plasticised PVC.

The present invention also provides a process for preparing the halogen-free polymeric composition defined above which includes mixing

- 30 (a) at least two metallocene catalysed olefin polymers and/or copolymers wherein at least one of the olefin polymers and/or copolymers is elastomeric; and  
(b) an effective amount of at least one filler which is capable of providing the polymeric composition  
35 with flame retardant properties substantially similar to that of plasticised PVC.

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The term "metallocene catalysed olefin polymers and/or copolymers" is used herein in its broadest sense to refer to olefin polymers and/or copolymers produced using a metallocene catalyst. Suitable metallocene catalysed  
5 olefin polymers and/or copolymers include ethylene polymers and/or copolymers such as polyethylene and ethylene based alkene or alphaolefin copolymers, for example, ultra low density polyethylene (ULDPE), very low density polyethylene (VLDPE), ethylene propylene copolymers, ethylene butene  
10 copolymers, ethylene hexene copolymers and ethylene octene copolymers. Commercially available metallocene catalysed olefin polymers and/or copolymers have a minor amount preferably less than about 18%, more preferably less than about 15% by weight of a C<sub>3</sub> or higher alkene such as hexene  
15 or octene. Preferred metallocene catalysed olefin polymers and/or copolymers are polyethylene, ethylene hexene copolymers and ethylene octene copolymers, more preferably ethylene octene copolymers.

It will be understood that metallocene polymers  
20 and/or copolymers are also prefixed in the art by "m" e.g., metallocene catalysed VLDPE would be referred to as mVLDPE.

The metallocene catalysed olefin polymers and/or copolymers may be conveniently classified into polyolefin elastomers (POE) and polyolefin plastomers (POP).  
25 Elastomers and plastomers can be characterised by means of specific gravity (S.G.) and other properties such as the differential scanning calorimetry (DSC) melting peak, Shore A hardness and elasticity modulus.

It will be appreciated that such properties will  
30 vary depending on the type of metallocene catalysed olefin polymer and/or copolymer and its method of manufacture. However, generally polyolefin elastomers (POE) are elastomeric and highly flexible and polyolefin plastomers (POP) are plastomeric or thermoplastic elastomeric and  
35 flexible.

For example, polyolefin elastomers (POE) composed of ethylene octene copolymers having less than about 18%

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octene such as Engage 8401 marketed by Dow DuPont Elastomers have a S.G. of up to about 0.885, DSC melting point up to about 80°C, Shore A hardness up to about 86 Shore A and an elasticity modulus of up to about 25 MPa.

5 Polyolefin plastomers (POP) composed of the same ethylene octene copolymers such as Engage 8440 have a S.G. more than about 0.886, DSC melting peak of above about 81°C, Shore A hardness of above about 87 Shore A and an elasticity modulus of above about 30 MPa. However, there is sometimes

10 confusion in the marketplace as to whether particular polyolefins are classified as elastomers or plastomers. Such polyolefins for example, Engage 8440 as described above is classified as a POE and Affinity 1440 which is exactly the same product is classified as POP, will

15 hereinafter be referred to in this specification as "POP/POE" or "POE/POP".

Preferably component (a) of the composition of the present invention contains at least one metallocene catalysed polyolefin elastomer (POE) and at least one

20 metallocene catalysed polyolefin plastomer (POP), preferably the metallocene catalysed polyolefin elastomer is present in a proportion of about 30% or more, more preferably about 50% or more based on the total amount of component (a).

25 Ideally, the metallocene catalysed olefin polymers and/or copolymers have a S.G. in the range of from about 0.850 to about 0.915, preferably about 0.860 to about 0.90 and more preferably about 0.88 to about 0.90; a melt flow index in the range of from about 0.5 to about 50 and

30 preferably about 1 to about 30; a Shore Hardness A in the range of from about 66 to about 96 Shore A and preferably about 85 to about 93 Shore A; and a DSC melting peak in the range of from about 49 to about 107°C, preferably about 65 to about 98°C and more preferably about 70 to about 92°C.

35 Component (a) may also preferably contain up to about 35% of a non-metallocene and/or metallocene catalysed olefin copolymer elastomer or a rubbery flexible copolymer

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which imparts even greater flexibility to the composition and in the case of some copolymers a further improved flame retardance. Suitable elastomers include synthetic rubbers having at least about 25% comonomer such as ethylene  
5 propylene copolymers or terpolymers, for example, EPR, EPM, ethylene propylene diene rubber (EPDM) and/or ethylene vinyl acetate copolymer (EVA) having a vinyl acetate component of about 25 to about 70%, preferably about 30 to about 45%. Such synthetic rubbers are generally known as  
10 classical rubbers made with conventional catalysts, however they can also be metallocene catalysed.

Component (a) may further contain from about 0.1 to about 15 PHR (parts per hundred parts of polymer), preferably from about 2 to about 10 PHR and more preferably  
15 from about 4 to about 6 PHR of a maleic anhydride modified ethylene copolymer or graft of maleic anhydride on ethylene propylene rubber, ethylene vinyl acetate, polypropylene or polyethylene of all grades and types including high density polyethylene (HDPE), medium density polyethylene (MDPE),  
20 low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density polyethylene and (ULDPE) and very low density polyethylene (VLDPE), for example, maleic anhydride grafted polyethylene (MAH-PE).

It will be understood that other polymers,  
25 copolymers, elastomers and/or plastomers can be added in order to enhance the properties of the composition. Such polymers, copolymers, elastomers and/or plastomers may include other ethylene, propylene or butylene polymers and copolymers, ethylene acrylic copolymers, ethylene acrylic  
30 ester copolymers and rubbers such as silicone rubber, nitrile butadiene rubber (NBR) and butyl rubber (BR). These other polymers, copolymers, elastomers and/or plastomers may be added in amounts of up to about 30 PHR, preferably no more than about 20 PHR, more preferably no  
35 more than about 10 PHR so as to minimise costs.

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In a preferred embodiment, component (a) of the composition includes at least about 30 PHR of at least one metallocene catalysed polyolefin elastomer (POE), for example, an ethylene C<sub>6</sub>-C<sub>8</sub> alphaolefin elastomer with an S.G. of up to about 0.885, preferably at least about 40 PHR, more preferably at least about 50 PHR for more flexible compositions and most preferably at least about 60 PHR for an even more flexible compositions with the remainder being at least one metallocene catalysed polyolefin plastomer (POP) or plastomer with elastomer behaviour (with an S.G. of above about 0.885).

In another preferred embodiment which provides a more flexible composition, component (a) includes at least about 20% of an olefin copolymer elastomer and/or a rubbery, flexible copolymer and even more preferably at least about 33% of a synthetic rubber with the remainder being at least one metallocene catalysed polyolefin elastomer and at least one metallocene catalysed polyolefin plastomer, for example, about 40% of POE about 40% of POP or POE and about 20% of a synthetic rubber/polyolefin copolymer elastomer or another flexible, rubbery copolymer, even more preferably about 30 to about 40% of POE, about 30 to about 35% of POP or POE (S.G. above about 0.886) and about 30 to about 35% of synthetic rubber/polyolefin copolymer elastomer.

Component (b) may contain one or more fillers provided that at least one has flame retardant properties. Preferably, the flame retardant filler is capable of developing H<sub>2</sub>O and/or H<sub>2</sub>O and CO<sub>2</sub> in an endothermic process in the case of a fire. Suitable fillers include inorganic and/or mineral fillers such as alkaline earth metal carbonates, talc, clays which may be calcined, kaolin, huntite and/or hydromagnesite. The fillers may be also be used in combination with coatings, for example, stearic acid, stearates such as calcium stearate, vinyl silanes and/or titanates. While such coatings may be used to coat the fillers, it will be appreciated that they can also be

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added simultaneously, sequentially and/or separately with the fillers. The fillers may be present in an amount of about 80 to about 250 PHR, preferably about 100 to about 220 PHR and more preferably about 150 to about 200 PHR.

5 Preferably the filler is huntite and hydromagnesite which may be in the form of a natural mineral, compound or mixture such as products marketed under the trade names of ULTRACARB or SECUROC which costs less than the currently used aluminium or magnesium  
10 hydroxide, but possesses substantially similar flame retardance.

Huntite is a magnesium calcium carbonate having the formula  $Mg_3Ca(CO_3)_4$  and hydromagnesite is a hydrated magnesium carbonate having the formula  $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ .  
15 The huntite and hydromagnesite can also be mixed artificially in proportions of preferably about 40:60 or about 60:40. The gross molecular formula of the huntite hydromagnesite is  $Mg_3Ca(CO_3)_4 \cdot Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ . The huntite/hydromagnesite specific surface measured by  
20 nitrogen absorption of preferably 4-12 m<sup>2</sup>/g, more preferably of 5-10 m<sup>2</sup>/g) and is preferably a coated grade, e.g. with stearic acid or calcium stearate. The particle size preferably is about 50% below about 1 micron.

The main advantage of the huntite and  
25 hydromagnesite filler is that it develops  $H_2O$  and  $CO_2$  in a broader temperature range of about 220 to about 600°C than aluminium and/or magnesium hydroxide and therefore gives a good protection over the range of temperatures which occurs during a fire. Furthermore, the processing temperatures of  
30 huntite and hydromagnesite are about 30 to 40°C higher than aluminium hydroxide, ie., the former can be processed up to about 200 to about 220°C where as the latter can be processed at up to about 160 to about 180°C so as to avoid emission of water vapour that could cause porosity and  
35 voids. This is a significant advantage for huntite and hydromagnesite allowing higher processing speeds.



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Another preferred low cost filler combination is huntite and hydromagnesite with an alkaline earth metal carbonate which may be hydrated, for example, magnesium or calcium carbonate such as products marketed under the trade name OMYACARB 2 or 2T where more CO<sub>2</sub> is developed in the higher temperature range in a synergistic effect. Both the huntite and hydromagnesite and the alkaline earth metal carbonate are present in an amount of about 75 to about 150 PHR, preferably about 75 to about 120 PHR and more preferably about 75 to about 100 PHR each.

The huntite and hydromagnesite and calcium carbonate in combination with POE/POP's result in lower heat deformation, that is, better resistance to pressure at high temperatures (higher resistance to heat compression) than that of aluminium hydroxide. The fillers and compositions of the present invention including the substitutions with aluminium or magnesium hydroxide have excellent, low heat compression at about 90°C although they are thermoplastic i.e., non-cross-linked or thermoelastic and composed of POE's which melt up to below about 80°C and POP's which melt at about 95°C. Such excellent, low heat compression is normally obtained only with cross-linked compositions which are of higher cost as a consequence of both the additional processing step of cross-linking and the use of cross-linking additives.

The huntite and hydromagnesite and/or the alkaline earth metal carbonate can be substituted as a flame retardant wholly or partly by aluminium and/or magnesium hydroxide, but with consequently higher costs further increasing the flame retardance properties of the composition. Surprisingly amounts of, for example, 80 PHR of huntite and hydromagnesite with 80 PHR of calcium carbonate result in an LOI (limiting oxygen index) similar to that of plasticised PVC.

Other flame retardant materials and/or char forming additives may be included in the composition, for example, borates and metaborates such as zinc borate or

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metaborate, glass beads or particles, silica, silicon dioxide, compounds of silicon dioxide with other metal oxides in amounts of about 1 to about 30 PHR, preferably about 3 to about 20 PHR, more preferably about 5 to about 15 PHR, most preferably about 5 to about 10 PHR depending on the type of additive.

It will be appreciated that one or more additives known in the art of polymer processing can also be included in the composition. Suitable additives include

10 antioxidants, for example, phenolic antioxidants such as SANTONOX R marketed by Monsanto and IRGANOX 1010 which is pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate or IRGANOX 1035 which is octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate

15 marketed by Ciba-Geigy or aminic antioxidants such as Vulcanox HS and Flectol H which are polymerised 2,2,4-trimethyl-1,2-dihydroquinoline; metal deactivators and/or copper inhibitors, for example, hydrazides such as oxalic acid benzoyl hydrazide (OABH) or Irganox 1024 which is

20 2,3-bis-((3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl))propiono hydrazide; UV absorbers, for example Tinuvin or HALS type UV absorbers; foaming or blowing agents which may be either endothermic or exothermic for example, p,p-oxybis benzene-sulfonyl-hydrazide, azo-iso-butyro-nitrile and azodicarbonamide; processing and/or

25 thermal stabilisers, for example tris (2,4-ditert-butylphenyl) phosphite (phosphite based), pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), octadecyl-3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,

30 3,3',3',5,5',5'-hexa-tert-butyl-a,a',a'-(mesitylene-2,4,6-triyl)tri-p-cresol (phenolic based) and dioctadecyl-3,3'-thiodipropionate (thioester based); and pigments, for example, inorganic pigments such as titanium dioxide and carbon black and organic pigments. The metal deactivators

35 and/or copper inhibitors are particularly useful when the polymeric composition is in contact with copper conductors or wire.

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The additives may be present in amounts in the range of about 0.1 to about 4 PHR, preferably about 0.5 to about 3 PHR and more preferably about 1 to about 2 PHR for higher performance in ageing and about 0.1 to about 0.2 PHR for a good or acceptable ageing performance depending on the application or use of the intended product. The metal deactivators can be added in proportions of about 0.1 to about 0.5 PHR, preferably about 0.1 to about 0.3 PHR, more preferably about 0.15 to about 0.25 PHR.

The polymers used for component (a) are preferably granulated, pelletised and/or powderised. In the case of rubber, preferably cut or diced. Components (a) and (b) can then be pre-mixed or added simultaneously, sequentially and/or separately to any suitable known apparatus, such as roll mills, internal mixers or continuous mixers for example twin screw mixers.

The final polymeric composition of the invention can be formed by any suitable known process including injection moulding, blow moulding, compression moulding, extrusion or calendering into articles such as tubes, pipes, cables, profiles, sheets, films and pre-forms.

The polymeric compositions of the invention may optionally be cross-linked by adding cross-linking catalysts such as organic peroxides, for example, dicumylperoxide, di-tert-butyl peroxide, and/or di-tert-butyl cumyl peroxide. They can also be radiation cross-linked using gamma-radiation or high energy electron beam radiation. The compositions may also be cross-linked after grafting component (a) or the composition with about 1 to about 2 PHR of a vinyl-silane, for example, vinyl alkoxyl silane with the aid of about 0.1 to about 0.2 of an organic peroxide, for example dicumyl-peroxide (DICUP) or di-tert-butyl peroxide (DTBP). Catalysts for cross-linking include DBTDL (di-butyl-tin-dilaurate) or dioctyl-tin-dilaurate (DOTDL) in an amount of about 0.1 to about 0.25 PHR, preferably about 0.1 to about 0.15 PHR.

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The cross-linking of the peroxide cross-linkable composition or the resulting products may be conducted in steam or nitrogen under pressure at elevated temperatures, higher than the decomposition temperatures of the peroxides used to form free radicals. Radiation cross-linking is carried out at room temperatures. Silane cross-linking is carried out in the presence of water, steam or moisture at ambient or preferably at higher temperatures of up to about 90 to about 100°C.

The non-cross-linked polymeric compositions are thermoplastic and still pass heat compression tests at 80°C and/or 90°C and some even 100°C. This is unexpected as the preferred metallocene catalysed olefin polymers and/or copolymers have melting temperatures (DCS melting peaks) of about 60°C to about 98°C and more preferably about 75 to about 95°C, however the compositions of the present invention can pass the heat compression tests to AS (Australian Standard) 1660 which is also called pressure test at elevated temperatures and the deformation is to be lower than 50%. The compositions to the invention contain up to about 50 to about 60 PHR of POE with lower melting temperatures below about 80 or about 90°C and they are not cross-linked, however surprisingly they pass the hard heat compressions tests to AS 1660 at about 90°C (or about 80°C or about 100°C depending on the composition requirements).

The limiting oxygen index (LOI) of the polymeric compositions, which is a measure of their flame retardance is typically in the range of from about 24 to about 30%. The LOI ranges required to predict for various polymer systems whether they may pass real standardised flame test e.g. on single cables are quite different and indicative only for the development within the same system, depending on the polymers and/or copolymers, flame retardant filler and/or additive systems. The flame test to a standard is the measure for flame retardance. Regular plasticised PVC is in the range of about 26% to 28% LOI.

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The polymeric compositions of the present invention possess advantageous properties including being low cost, anti-fogging, non-halogenated, non-corrosive and having reduced toxicity and low smoke formation as far as combustion gases are concerned compared with plasticised PVC. It will also be appreciated that the properties such as hardness, softness, flexibility, tensile strength, elongation, flame retardance and resistance to compression can be adapted depending on the desired application and without the need to include the additives contained in plasticised PVC such as phthalate plasticisers and lead thermal stabilisers which have possible physiological effects.

Examples of applications of the polymeric composition include:

Electrical and optical: cables, wires and fibre such as power cables, building wires, data cables and communication cables;

Floor coverings: sheets or tiles which may be laminated or in combination with textiles, industrial mats, carpets, used in buildings, transport, vehicles;

Automotive: mudflaps, trays, seals, fabrics, soft feel coverings, console, sound/noise attenuation;

Buildings: seals, weather shields, flooring, panel trims, window seals, cladding and floormats; and

General: flexible tubing, hose, artificial leather, laminated films or sheets with or without textile backing.

Thus, the present invention further provides articles which are composed wholly or partly of the polymeric composition defined above.

Examples of compositions according to the invention and physical properties of the compositions are set out below. These examples are not to be construed as limiting the invention in any way.

Most of the compositions set out below have been tested to determine their flame retardant properties by the

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LOI expressed in % which gives some indication of flame retardance. Some of the compositions have been used to produce cable sheathing, insulated cores and/or sheathing or jacketing.

5                   2 or 3 core building wires to Australian Standard, eg. flat building wires have been produced by extrusion. The metallic copper conductors of the cores were insulated with either flame retardant and/or non-flame retardant compositions from an example of this invention or  
10 just regular non-flame retardant XLPE and sheathed with compositions of the invention.

The sample sheathed cable was placed vertically to IEC 332 part A or to AS 1660 part 5 to pass the single bunsen burner test.

15                   The flame tests on samples of the product are more relevant to check the flame retardance than the LOI test.

In the following examples, a combination of at least two metallocene catalysed polymers were used: a POE  
20 (Engage 8401 and/or Engage 8003) with an S.G. of 0.885 and a POP/POE with an S.G. of 0.897 (Engage 8440). The amounts quoted in the examples are expressed in PHR.

The compositions of the examples were made on laboratory mills and/or continuously mixing plant machinery  
25 twin screw mixers e.g. on contra-rotating mixer with twin screws of 80mm and on co-rotating twin screw mixers of 53 and/or 83 mm diameter. The compositions were made by pre-mixing the polymer granules/pellets with the filler powders in a pre-mixer and which were then fed into the hopper of  
30 the twin screw mixer (this could result in some slight separation of the components in the hopper and possibly some variation in the results), larger factory equipment with several ports of entrance for the ingredients allows a variety of filling sequences, e.g. the pre-mixed polymers  
35 in the hopper of the twin screw extruder, forming a melt and then adding the filler in the second feeding port and

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possibly another part in the third feeding port and thereby more homogenous compounds with further improved results.

Internal mixers, for example of the Banbury type may also be used alternatively in batch processing where  
5 the components are added either all together or in sequences, i.e., either the polymers first and fillers later or by the upside down method where the fillers are added first followed by the polymers. Single screw  
10 extrusion mixing machines with mixing parts in the cylinder of Buss-Ko-Kneader type for continuous mixing could also be used.

The samples made on the laboratory mills and/or continuously mixed on the twin screw mixers were then granulated or pelletised. The granules were either  
15 extruded into tapes on a laboratory extruder and/or pressed in a press and/or the granules were also injection moulded and then tested. In the case of injection moulded plaques, an average of the mechanical test results (in longitudinal and transversal direction) is shown.

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## Note:

Melting points to DSC melting peak are 76°C for 8401 and 95°C (for 8440) - yet the composition or plaques and/or cable samples passes the toughest test to Australian

- 5 Standard of pressure at high temperature or hot deformation or heat compression AS 1660 of hot deformation at 90°C for a temperature rating of 90°C (the maximum permitted is 50%). The test was also passed at 100°C.

10 EXAMPLE 3INSULATION

POE (Engage 8401)	- 50
POP/POE (Engage 8440)	- 50
MAH/LDPE	- 5
15 ULTRACARB C5-10	- 100
Tensile strength	- 10.8Mpa
Elongation	- 320%
Shore C	- 75%
20 LOI*	- 24%

## \* Note

- Adequate for insulation of cable cores i.e., insulation of metallic conductors as insulation in general does not
- 25 require a higher flame retardance. It contributes to a higher flame retardance of the whole cable where the core(s) is/are attached with a flame retardant sheathing or jacketing composition according to the invention.

30 EXAMPLE 4INSULATION

POE (Engage 8401)	- 50
POP/POE (Engage 8440)	- 50
MAH/LDPE	- 5
35 HYDRAL 710*	- 100

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	Tensile strength	- 12.6Mpa
	Elongation at break	- 520%
	Shore C	-67
	Hot deformation at 90°C	- 35%
5	LOI	- 25.5%

\* MARTINAL OL-104LE (low electrolyte) can also be used for insulation grade

10 EXAMPLE 5

	POP/POE (Engage 8440)	- 40
	POE (Engage 8401)	- 40
	EPR (DUTRAL CO.038)	- 20
	FUSABOND (MAH-PE)	- 5
15	ULTRACARB C5-10	- 100
	OMYACARB 2T	- 100
	ANTIOXIDANT/IRGANOX 1010 MASTERBATCH	- 0.2

	Tensile Strength	- 8.7 Mpa
20	Elongation, Min.	- 160
	Shore C	-78
	Shore D instant	- 57
	Shore D instant after 15 seconds	- 44
	LOI	- 24%

25

EXAMPLE 6

	POP/POE (Engage 8440)	- 33.3
	POE (Engage 8401)	- 33.3
	EPR (DUTRAL CO.038)	- 33.3
30	FUSABOND (MAH-PE)	- 5
	ULTRACARB C5-10	- 100
	OMYACARB 2T	- 100
	ANTIOXIDANT 1010 MB	- 0.2

35	Tensile Strength	- 7.7
	Elongation, Min.	- 220
	Elongation, Max.	- 265

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	Shore C	- 76
	Shore D instant	- 54
	Shore D instant after 15 seconds	- 44
	Hot deformation at 90°C	- 18%
5	LOI	- 24%

Arch test very good (in-house test) a strip was bent, folded and placed as a V inverted, i.e.  $\Lambda$  on the table. Very good result, very flexible if it laid flat in 1 minute. This test was introduced to test the flexibility of the composition in plaque or strip form.

EXAMPLE 7

	POP/POE (Engage 8840)	- 40
15	POE (Engage 8401)	- 40
	ELVAX 4260	- 20
	ULTRACARB C5-10	- 100
	OMYACARB 2T	- 100
	ANTIOXIDANT (IRGANOX 1010 in a MB)	- 0.2
20		
	Tensile strength	- 6.7 Mpa
	Elongation at break	- 310%
	Shore C	- 77
	Shore D instant	- 61
25	Shore D instant after 15 seconds	- 53
	LOI	- 26%

## Note:

EVA (ELVAX 4260) included as 20 PHR into the total of 100 PHR of polymer, increases the LOI to 26%, vs. 24% with 20 PHR of EPR DUTRAL CO.

(Also refer to increase of LOI with EVA in Example 10 to 29% vs. 24% with 33 PHR of EPR in Example 9)

35

Note: MB means that 0.2 Irganox 1010 was added in form of a masterbatch.

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EXAMPLE 8

	POP/POE (Engage 8440)	- 33.3
	POE (Engage 8401)	- 33.3
5	EVA (45% VA) e.g. (LEVAPREN 450)	- 33.3
	MAH-PE (FUSABOND)	- 5
	ULTRACARB C5-10	- 75
	OMYACARB 2T	- 75
	ANTIOXIDANT IRGANOX 1010 MB	- 0.2
10		
	Tensile Strength	- 7.5 MPa
	Elongation at break, Min.	- 225%
	Elongation at break, Max.	- 265%
	Shore C	- 74
15	Shore D instant	- 43
	Shore D instant after 15 seconds	- 34
	Hot deformation at 90°C	- 16%
	Arch Test	- Very Good
	LOI	- 26%
20		
	The formation of Example 8 seems to be very good for flexible building wire sheath, in particular for their flexibility. The highly flexible sheath also passed the bunsen burner test on a vertical building wire.	

25

EXAMPLE 9

	POP/POE (Engage 8440)	- 33.3
	POE (Engage 8401)	- 33.3
	EPR (DUTRAL CO.034)	- 33.3
30	MAH-PE (FUSABOND)	- 5
	ATH (MARTINAL 104LE)	- 80
	OMYACARB 2T	- 80
	ANTIOXIDANT/IRGANOX 1010 MB	- 0.2
35		
	Tensile Strength	- 7 MPa
	Elongation, Min.	- 125%
	Elongation, Max.	- 150%

- 20 -

	Shore C	- 69
	Shore D instant	- 48
	Shore D instant after 15 seconds	- 38
	Hot deformation at 90°C	- 25%
5	LOI	- 24%

## Note:

The excellently low hot deformation performance is remarkable and unexpected in such a soft flexible and non-cross-linked thermoplastic compound.

EXAMPLE 10

	POP/POE (Engage 8440)	- 33.3
	POE (Engage 8401)	- 33.3
15	EVA (45% VA) (LEVAPREN 450)	- 33.3
	MAH-PE (FUSABOND)	- 5
	ATH (MARTINAL 104LE)	- 80
	OMYACARB 2T	- 80
	ANTIOXIDANT/IRGANOX 1010 in a MB	- 0.2
20		
	Tensile Strength	- 9.5
	Elongation min	- 200%
	Elongated at break max	- 250%
	Shore D instant	- 53
25	Shore D instant after 15 seconds	- 43
	LOI	- 28%

## Note:

Comparing Example 9 and Example 10 one can see:

- 30 - DUTRAL CO.034 vs. LEVAPREN 450
- The compound with EPR DUTRAL is softer than with EVA (LEVAPREN)
- The tensile strength with EVA in Example 10 is higher than with EPR
- 35 - The LOI is increased from 24 to 28 (and 29 was also measured on another sample) by the EVA vs. the EPR.

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EXAMPLE 11

	POE (Engage 8401)	
	POP/POE (Engage 8440)	- 50
5	MAH/LDPE	- 15
	ULTRACARB C5-10	- 150
	OMYACARB 2T	- 50
	Shore D instant	- 56
10	Shore D after 15 seconds	- 48
	LOI	- 27%

## Note:

This compound has almost the same LOI as example 12 which  
15 also has additional EVA (Elvax).

EXAMPLE 12

	POE (Engage 8401)	- 50
	POP/POE (Engage 8440)	- 50
20	ELVAX 4260 (25%VA)	- 15
	MAH LDPE	- 15
	ATH HYDRAL 710	- 150
	OMYACARB 2T	- 50
	IRGANOX 1010	- 0.3
25	Tensile Strength	- 11.7 MPa
	Elongation at break	- 130%
	Shore D instant	- 59
	Shore D after 15 seconds	- 51
30	LOI	- 28%

EXAMPLE 13

	POE (Engage 8401)	- 50
	POP/POE (Engage 8440)	- 50
35	MAH-LDPE	- 15
	ULTRACARB C5-10	- 120
	OMYACARB 2T	- 50

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	Tensile Strength	- 11.8 MPa
	Elongation at break	- 125%
	Shore D instant	- 61
5	Shore D after 15 seconds	- 53
	LOI	- 26.5%

EXAMPLE 14

	POE (Engage 8401)	- 50
10	POP/POE (Engage 8440)	- 50
	MAH-LDPE (FUSABOND)	- 5
	ULTRACARB C5-10	- 100
	OMYACARB 2	- 100
15	Tensile Strength	- 6.7 MPa
	Elongation at break Min	- 125%
	Elongation at break Max.	- 225%
	Shore C	- 74
	Shore D instant	- 51
20	Shore D after 15 seconds	- 41
	Heat deformation at 90C	- 7%

EXAMPLE 15

	POP/POE (Engage 8440)	- 33.3
25	POE (Engage 8401)	- 33.3
	ELVAX 4260	- 33.4
	USTRACARB C5-10	- 100
	OMYACARB 2	- 100
30	Tensile strength	- 8.5 MPa
	Elongation at break Min.	- 125%
	Elongation at break Max.	- 145%
	Shore C	- 76
	LOI	- 26%

35

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Note:

OMYACARB 2 is untreated, improved dispersion and mechanical properties with addition of 1% stearic acid or calcium stearate.

5

EXAMPLE 16

	POP/POE (Engage 8440)	- 50
	POE (Engage CL8003)	- 50
	MAH-LDPE	- 5
10	ULTRACARB C5-10	- 100
	OMYACARB 2	- 150
	Tensile strength	- 6 MPa
	Elongation at break Min.	- 100%
15	Elongation at break Max.	- 135%
	Shore D	- 51
	LOI	- 26%

Note:

- 20 Engage 8003 or CL8003 has an s.g. of 0.885 and MFI = 1.  
(Engage 8401 has the same s.g. and MFI = 30).

EXAMPLE 17

	POP/POE (Engage 8440)	- 50
25	POE (Engage CL8003)	- 50
	MAH-LDPE (XUS Dow)	- 5
	OMYACARB 2	- 150
	ATH (5m2/g untreated)	- 100
	IRGANOX 1010	- 0.3
30	Tensile Strength	- 6.9MPa
	Elongation at break Min.	- 120%
	Elongation at break Max.	- 135%
	Shore D	- 57
35	LOI	- 27%



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EXAMPLE 18

	POP/POE (Engage 8440)	- 50
	POE (Engage 8003)	- 50
	MAH-LDPE (XUS)	- 5
5	OMYACARB 2	- 100
	ATH (5m2/g, untreated)	- 100
	IRGANOX 1010	- 0.3
	Shore D	- 50
	LOI	- 26%

10

EXAMPLE 19

	POP/POE (Engage 8440)	- 50
	POE (Engage 8401)	- 50
	MAH-LDPE (FUSABOND)	- 5
15	ATH (MARTINAL 104 or HYLRAL 710)	- 200
	IRGANOX 1010	- 0.2
	Tensile Strength	- 10.2/10.0
	Elongation at break Min.	- 130/125%
20	Elongation at break Max	- 170/150%
	Shore C	- 82/82
	Shore D instant	- 60/57
	Shore D (15 sec.)	- 52/49
	LOI	- 29%

25

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## CLAIMS:

1. A halogen-free polymeric composition including:
  - (a) at least two metallocene catalysed olefin  
5 polymers and/or copolymers wherein at least one of the  
olefin polymers and/or copolymers is elastomeric; and
  - (b) an effective amount of at least one filler  
which is capable of providing the polymeric composition  
with flame retardant properties substantially similar to  
10 that of plasticised PVC.
2. A composition according to claim 1 wherein the  
metallocene catalysed olefin polymer and/or copolymer is an  
ethylene polymer and/or copolymer.  
15
3. A composition according to claim 1 or claim 2  
wherein the metallocene catalysed olefin polymer and/or  
copolymer is polyethylene or an ethylene based alkene  
copolymer.  
20
4. A composition according to claim 3 wherein the  
polyethylene is ultra low density polyethylene (ULDPE) or  
very low density polyethylene (VLDPE).
- 25 5. A composition according to claim 3 wherein the  
ethylene based alkene copolymer has a C<sub>3</sub> or higher alkene.
6. A composition according to claim 3 or claim 5  
wherein the ethylene based alkene copolymer is an ethylene  
30 butene copolymer, ethylene hexene copolymer or ethylene  
octene copolymer.
7. A composition according to claim 3, claim 5 or  
claim 6 wherein the ethylene based alkene copolymer is an  
35 ethylene hexene copolymer or an ethylene octene copolymer.

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8. A composition according to any one of claims 3 to 7 wherein the ethylene based alkene copolymer is an ethylene octene copolymer.

5 9. A composition according to any one of claims 3 to 8 wherein the amount of alkene present in the ethylene based alkene copolymer is less than about 18%.

10 10. A composition according to any one of the preceding claims wherein component (a) contains at least one metallocene catalysed polyolefin elastomer (POE) and at least one metallocene catalysed polyolefin plastomer (POP).

15 11. A composition according to claim 10 wherein the metallocene catalysed polyolefin (POE) elastomer is present in an amount of about 30% or more based on the total amount of component (a).

20 12. A composition according to any one of the preceding claims wherein the metallocene catalysed olefin polymer and/or copolymer has an S.G. in the range of about 0.850 to about 0.915.

25 13. A composition according to claim 12 wherein the metallocene catalysed olefin polymer and/or copolymer has an S.G. in the range of about 0.860 to about 0.90.

30 14. A composition according to claim 12 or claim 13 wherein the metallocene catalysed olefin polymer and/or copolymer has an S.G. in the range of about 0.88 to about 0.90.

35 15. A composition according to any one of the preceding claims wherein the metallocene catalysed olefin polymer and/or copolymer has a melt flow index in the range of about 0.5 to about 50.

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16. A composition according to claim 15 wherein the metallocene catalysed olefin polymer and/or copolymer has a melt flow index in the range of about 1 to about 30.
- 5 17. A composition according to any one of the preceding claims wherein the metallocene catalysed olefin polymer and/or copolymer has a Shore Hardness A in the range of about 66 to about 96 Shore A.
- 10 18. A composition according to claim 17 wherein the metallocene catalysed olefin polymer and/or copolymer has a Shore Hardness A in the range of about 85 to about 93 or Shore A.
- 15 19. A composition according to any one of the preceding claims wherein the metallocene catalysed olefin polymer and/or copolymer has a DSC melting peak in the range of about 49 to about 107°C.
- 20 20. A composition according to claim 19 wherein the metallocene catalysed olefin polymer and/or copolymer has a DSC melting peak in the range of about 65 to about 98°C.
21. A composition according to claim 19 or claim 20,  
25 wherein the metallocene catalysed olefin polymer and/or copolymer has a DSC melting peak in the range of about 70 to about 92°C.
22. A composition according to any one of the  
30 preceding claims wherein component (a) further contains up to about 35% of a non-metallocene and/or metallocene catalysed olefin copolymer elastomer with at least about 20% comonomer.
- 35 23. A composition according to claim 22 wherein the elastomer is a synthetic rubber.

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24. A composition according to claim 23 wherein the synthetic rubber is ethylene propylene rubber (EPR, EPM), ethylene propylene diene rubber (EPDM) and/or ethylene vinyl acetate copolymer (EVA).

5

25. A composition according to claim 24 wherein the ethylene vinyl acetate copolymer has a vinyl acetate component of about 25 to about 70%.

10 26. A composition according to claim 25 wherein the ethylene vinyl acetate copolymer has a vinyl acetate component of about 30 to about 45%.

15 27. A composition according to any one of the preceding claims wherein component (a) further contains a maleic anhydride modified ethylene copolymer or a graft of maleic anhydride on ethylene propylene rubber or polyethylene.

20 28. A composition according to claim 27 wherein the amount of a maleic anhydride modified ethylene copolymer or graft of maleic anhydride on ethylene propylene rubber, ethylene vinyl acetate, polypropylene or polyethylene is about 0.1 to about 15 PHR.

25

29. A composition according to any one of the preceding claims wherein component (a) further contains other polymers, copolymers, elastomers and/or plastomers.

30 30. A composition according to claim 29 wherein the other polymers, copolymers, elastomers and/or plastomers are other ethylene, propylene or butylene polymers and copolymers, ethylene acrylic copolymers, ethylene acrylic ester copolymers and rubbers.

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31. A composition according to claim 30 wherein the rubber is silicone rubber nitrile butadiene rubber (NBR) or butyl rubber (BR).

5 32. A composition according to claim 29 to claim 31 wherein the amount of other polymers, copolymers, elastomers and/or plastomers is up to about 30 PHR.

10 33. A composition according to any one of the preceding claims wherein component (a) includes at least about 30 PHR of at least one metallocene catalysed polyolefin elastomer (POE) with an S.G. of less than about 0.885 with the remainder being at least one metallocene catalysed polyolefin plastomer (POP).

15

34. A composition according to any one of the preceding claims wherein component (a) includes at least about 20% of an olefin copolymer elastomer and/or rubbery, flexible copolymer with the remainder being at least one  
20 metallocene catalysed polyolefin elastomer (POE) and at least one metallocene catalysed polyolefin plastomer (POP).

35. A composition according to claim 34 wherein component (a) includes about 40% of POE about 40% of POP or  
25 POE and about 20% of a synthetic rubber/polyolefin copolymer elastomer.

36. A composition according to any one of the preceding claims wherein the filler is an inorganic and/or  
30 mineral filler.

37. A composition according to claim 36 wherein the filler is an alkaline earth metal carbonate, clays which are optionally calcined, talc, kaolin, huntite and/or  
35 hydromagnesite.

- 30 -

38. A composition according to claim 36 or claim 37, wherein the filler is used in combination with and/or coated with stearic acid, stearate, vinyl silanes and/or titanates.

5

39. A composition according to claim 39 wherein the stearate is calcium stearate.

40. A composition according to any one of claims 36 to 39, wherein the filler is huntite and hydromagnesite.

10

41. A composition according to any one of claims 36 to 40, wherein the filler is a combination of huntite and hydromagnesite with an alkaline earth metal carbonate.

15

42. A composition according to claim 41 wherein the alkaline earth metal carbonate is magnesium carbonate and/or calcium carbonate.

43. A composition according to any one of claims 36 to 42 wherein at least one of the filler is substituted wholly or partly by aluminium hydroxide and/or magnesium hydroxide.

20

44. A composition according to any one of claims 36 to 43, wherein the filler is present in an amount of about 80 to about 250 PHR.

25

45. A composition according to any one of the preceding claims which includes other flame retardant materials and/or char forming additives.

30

46. A composition according to claim 45, wherein the other flame retardant materials and/or char forming additives are borates, metaborates, glass beads or particles, silica, silicon dioxide and/or compounds of silicon dioxide with other metal oxides.

35

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47. A composition according to claim 45 or claim 46, wherein the amount of other flame retardant materials and/or char forming additives is about 1 to about 30 PHR.

5

48. A composition according to any one of the preceding claims which further includes other additives.

49. A composition according to claim 48 wherein the other additives are antioxidants, metal deactivators and/or copper inhibitors, UV absorbers, foaming or blowing agents, and/or pigments.

50. A composition according to claim 48 or claim 49 wherein the amount of other additives is about 0.1 to about 4 PHR each.

51. A composition according to any one of the preceding claims which is cross-linked.

20

52. A process for preparing the halogen-free polymeric composition defined in any one of claims 1 to 51 which includes mixing

(a) at least two metallocene catalysed olefin polymers and/or copolymers wherein at least one of the olefin polymers and/or copolymers is elastomeric; and

(b) an effective amount of at least one filler which is capable of providing the polymeric composition with flame retardant properties substantially similar to that of plasticised PVC.

30

53. A process according to claim 52 wherein components (a) and (b) are pre-mixed or mixed simultaneously, sequentially and/or separately.

35

54. A process according to claim 52 or claim 53 wherein the polymeric composition is cross-linked.



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55. An article which is composed wholly or partly of the polymeric composition defined in any one of claims 1 to 51.

5

56. An article according to claim 55 which is an electrical or optical part, cable, or wire; floor covering; automotive part; building part; tubing; hose; or artificial leather.

## INTERNATIONAL SEARCH REPORT

 International application No.  
**PCT/AU01/01226**

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>														
Int. Cl. <sup>7</sup> : C08L 23/04, 23/06, 23/08, C08K 3/26, 3/34														
According to International Patent Classification (IPC) or to both national classification and IPC														
<b>B. FIELDS SEARCHED</b>														
Minimum documentation searched (classification system followed by classification symbols)														
IPC: AS ABOVE														
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched														
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)														
WPAT & JAPIO; search terms: metallocene, olefin, filler														
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 5763501 A (BICKHARDT et al.) 9 June 1998 See column 3 line 13 to column 4 line 22 and the examples	1-56												
X	US 6107385 A (IMAHASHI) 22 August 2000 See column 3 lines 8-25 and the examples	1-56												
X	WO 00/26296 A (EXXON CHEMICAL PATENTS INC.) 11 May 2000 See page 7 lines 6-14 and the claims	1-56												
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex														
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Date of the actual completion of the international search 18 October 2001		Date of mailing of the international search report 23 OCT 2001												
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer ALBERT S. J. YONG Telephone No : (02) 6283 2160 												

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/01226

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent abstract Accession No. 98-033204/04, Class A17, BE 1010100 A (DSM NV) 2 December 1997 See abstract	1-56
X	Derwent abstract Accession No. 98-114862/11, Class A17, JP 10001573 A (MITSUI PETROCHEM IND CO LTD) 6 January 1998 See abstract	1-56

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU01/01226**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5763501	DE	19548681	EP	780207		
US	6107385	AU	24019/99	CN	1234413	EP	953599
		JP	2000017123	NO	991935	JP	11311352
WO	00/26296	AU	20204/00	EP	1124900	DE	59606681
		US	6070315				
BE	1010100	NONE					
JP	10001573	NONE					
END OF ANNEX							